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Giant diamagnetism of gold nanorods

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Abstract

The presence of giant diamagnetism in Au nanorods, NRs, is shown to be a possible consequence of field induced currents in the surface electrons. The distance, Δ, between quantum surface energy levels has been calculated as a function of the NRs radius. Note that those electrons occupying states for which $\Delta > k_B T$ are steadily orbiting with constant orbital moment. The diamagnetic response induced when a field is turned on remains constant during the time the field is acting. As the NRs radius increases, Δ decreases and accordingly the electron fraction available to generate constant currents decreases, consequently the surface diamagnetic susceptibility decreases towards its bulk value. The surface electronic motion induced by the axial applied field on electrons confined into a cylindrical surface accounts with extremely good quantitative agreement for the giant diamagnetism recently measured and reported.

Keywords: giant diamagnetism, gold nanorods, orbital magnetism

It has been recently reported that Au nanoparticles, NPs, with functionalized surfaces, exhibit a surprising magnetic behavior characterized by a giant paramagnetic or even a ferromagnetic-like response [1–11]. In previous articles it has been experimentally observed [1, 2, 4, 5] and theoretically predicted [12, 13] that the electronic structure of the NPs surface is modified by

effect of the binding with the capping molecules. In particular, the bond between thiolates and Au clusters was studied by using first principle calculations [13]. It has been also shown that quasi- free electrons confined in the surface of spherical shaped NPs can generally give rise to giant paramagnetism [11] when the Fermi level is sufficiently unfilled, what normally happens as a consequence of the modification of the Au surface band structure induced by the capping molecules. Previous experimental results have also confirmed the diamagnetic behaviour of Au NPs stabilized by means of a surfactant, tetraalkylammonium, that protects gold NPs with a weakly interacting dipole type binding that does not transform into paramagnetic the response of the surface [2]. In this case the Au NPs are diamagnetic like the bulk. This result indicates that the binding to some molecules does not change the sign of the bulk magnetic susceptibility.

Even though the details of the modification of the electronic structure and its dependence of the binding type of the capping molecules is a question open and thoroughly debated, a conclusion that can be inferred from these experiments turns out to be the outstanding influence of the surface magnetism on the overall NPs magnetic response. In fact the paramagnetic or ferromagnetic-like susceptibility exhibited by some Au NPs reflects the magnetism of the surface. The effect of the binding to the capping molecules modifies the magnetism of the surface. But the bare surface might exhibit a magnetic behaviour different to that of the bulk, as indicated in [11]. Electrons confined in spherical or cylindrical surfaces exhibit permanent orbital moments available to contribute to the susceptibility depending on its net value in the band. Note that this is not the case for electrons confined on plane surfaces. The net value of the angular moment can be affected by the binding that can drive changes from diamagnetism to paramagnetism. However, the unavoidable use of dispersant masks the natural magnetism of the surface. The only way to approach experimentally to the magnetic features of bare surfaces of Au NPs and/or NRs is to measure samples capped by molecules that do not modify strongly the electronic structure of the surface.

Van Rhee *et al* [14] have recently published a relevant article in which an experimental diamagnetic response more than one order of magnitude higher than that of bulk gold is reported for aligned Au NRs. They indicate that the origin of this unexpected magnetism as well as its differences observed between different types of nanoparticles, NPs, is not yet understood. They also indicate that modification of the surface electronic structure can be disregarded as the cause of the diamagnetic enhancement, because the electronic structure remains unchanged by the capping they used. They emphasize that the intriguing result is the strength of the observed susceptibility. To account for that, they suggest mesoscopic fluctuations that could give rise to oscillations in the susceptibility up to 100 times the Landau susceptibility of a bulk free electron gas [15]. Up to now, these oscillations has not been found experimentally in NPs.

The objective we pursue herein is to study the diamagnetic response in NRs. It is to be noted that the net diamagnetic currents analyzed below, are those induced in any metallic cylinder when an axial magnetic field is applied. Normally for macroscopic samples the current vanishes after a relaxation time of the order of $10^{-14}\,s$ at room temperature. It will be shown that for NRs a large fraction of surface electron can orbit steadily along the surface and around the field direction provided that the distance in energy, Δ, between their energy levels and the nearest ones is larger than k_BT. In this case the field momentum, $eBr/2$, absorbed by the electron when the field is turned on can not be transferred to the thermal bath. Under these conditions both diamagnetism and paramagnetism of the surface electrons can be much stronger than those corresponding to electrons localized in atoms due to the larger values of the radius of the orbit or to the large spontaneous orbital magnetic moments, respectively [11]. Thus, the spectrum of

quasi-free electron systems confined on a cylindrical surface or nanotube, NTs, its Fermi level and the distance between adjacent levels is briefly analyzed in order to ascertain the fraction number of the electrons available to contribute to the steady currents.

For the case of NTs, with height L and radius r, the eigenfunctions corresponding to quasi-free electrons can be written as:

$$\Psi(\varphi, z) = \frac{1}{\sqrt{\pi r L}} e^{in_\varphi \varphi} sin \frac{n_z \pi z}{L} \tag{1}$$

where n_φ and n_z account for the azimuthal and longitudinal quantum numbers, respectively. Note that n_φ corresponds to the axial magnetic quantum number.

The energies are:

$$E = \frac{h^2}{8m_{\text{eff}}}\left(\frac{n_z^2}{L^2} + \frac{n_\varphi^2}{\pi^2 r^2}\right) = \frac{h^2}{8m_{\text{eff}}\pi^2 r^2}\left(\psi^2 n_z^2 + n_\varphi^2\right) \tag{2}$$

where m_{eff} is the effective mass of the electrons and $\psi^2 = \pi^2 r^2/L^2$ is the square of the aspect ratio of the *NT*.

According to relation (2) the distance, $\Delta\left(n_\varphi\right)$, in energy between levels characterized by two successive n_φ eigenvalues and constant n_z, is given by

$$\Delta\left(n_\varphi\right) = \frac{h^2}{8m_{\text{eff}}\pi^2 r^2}\left(2n_\varphi + 1\right) = \frac{0.038}{m^* r^{*2}}\left(2n_\varphi + 1\right) eV \tag{3}$$

where m^* is the effective mass in units of the electron mass and r^* is the *NT* radius in nanometers. From (3) it is inferred that Δ is higher than the thermal energy, $k_B T$, if n_φ is larger than n_φ^c given by

$$n_\varphi^c(T) = k_B T \frac{m^* r^{*2}}{0.076} - \frac{1}{2} \tag{4}$$

$k_B T$ must be expressed in *eV*.

Equation (4) can be envisaged as the condition for an electron to be able to steadily circulate around the field with a constant orbital moment along the *NT* axis.

If the total number of electrons at the surface band is N and the maximum quantum number is $n_\varphi^{\max}$, the number of electrons, N^*, with n_φ, verifying $n_\varphi^{\max} \geqslant n_\varphi \geqslant n_\varphi^c$, shall be $N^* = \beta(T)N$. N^* is the number of electrons that circulate around the applied filed as long as the field remains applied.

The scaling factor $\beta(T)$ can be estimated as follows. First we should calculate $n_\varphi^{\max}$ as a function of the total number of surface electrons and the aspect ratio, ψ, of the *NT*. According to (2), the Fermi level is characterized by couple of values, n_φ, n_z such that $\left(\psi^2 n_z^2 + n_\varphi^2\right)$ is a constant, equal to $A_F = E_F \frac{8m_{\text{eff}}\pi^2 r^2}{h^2} = 52.6 m^* r^{*2} E_F$, where E_F should be given in *eV*. The $n_\varphi^{\max}$ value corresponds to the quantum number n_φ of the Fermi surface associated with $n_z = 1$, that thereby verifies $\psi^2 + n_\varphi^{2\max} = A_F$. At the Fermi level the following relationship between the couple of values n_φ, n_z holds

$$n_z\left(n_\varphi\right) = \frac{\sqrt{n_\varphi^{2\max} - n_\varphi^2}}{\psi} \tag{5}$$

where $n_z(n_\varphi)$ is the number of different n_z values, comprised between 1 and n_z, that are occupied for each n_φ lower than $n_\varphi^{\max}$. The total number of surface electrons N can be expressed after considering the spin degeneracy as

$$N = 2n_z(0) + 4\sum_{n_\varphi=1}^{n_\varphi^{\max}} n_z(n_\varphi) = 4\sum_{n_\varphi=0}^{n_\varphi^{\max}} n_z(n_\varphi) - 2n_z(0) \tag{6}$$

where the factor 4 in the second term accounts for the two allowed values n_φ and -n_φ. After taking into account equation (5) and by substituting the summation by a an integral in equation (6) the value of $n_\varphi^{\max}$, is estimated to be, within error of ± 1

$$n_\varphi^{\max} \cong \sqrt{N\psi} \cong \sqrt{\alpha}\frac{2\pi r}{a} \tag{7}$$

where N is the number of atoms on the cylindrical surface, approximately $2\frac{2\pi rL}{a^2}$ multiplied by the number of electrons, α, with which each atom contributes to the band. (a being the lattice constant, and the factor 2 has been included to take into account that there are two atoms per unit cell).

According to (3) and (7) the maximum Δ, corresponding to $n_\varphi^{\max}$ becomes

$$\Delta^{\max} \cong \frac{0.46}{m^* r^* a}\sqrt{\alpha}\,. \tag{8}$$

Secondly, according to (4), the number of electrons with n_φ comprised between 0 and n_φ^c is $1-N^*$ that can be written as

$$1 - N^* = 4\sum_{n_\varphi=0}^{n_\varphi^C} n_z(n_\varphi) - 2n_z(0). \tag{9}$$

Summing up, and taking into account equation (7), the following value for $\beta(T)$ is inferred

$$\beta(T) = 1 - \frac{n_\varphi^{c2}(T)}{n_\varphi^{\max\,2}} \cong 1 - \frac{3m^{*2}r^{*2}a^2}{2\alpha}\left(k_B T\right)^2. \tag{10}$$

The third term is obtained after taking into account (4) and (7).

For those N^* electrons circulating steadily is possible to estimate the diamagnetic moment, m_d, per atom induced by a field, B, applied along the rod axis [16] as given by

$$m_d = -\frac{e^2Br^2}{4m_{\text{eff}}}\alpha\beta(T). \tag{11}$$

The contribution to the diamagnetic moment of the Z inner electrons bound to any atom of the spherical surface should per atom be

$$m_d^{at} = -\frac{Ze^2Br_{at}^2}{6m}. \tag{12}$$

From (11) and (12) the diamagnetic susceptibility ratio, R_{NTs}, becomes:

$$R_{NTs} = \frac{\chi_d}{\chi_d^{at}} = \frac{3ra\alpha\beta m}{2Zr_{at}^2 m_{\text{eff}}} = \frac{3r^2\alpha\beta}{2Zr_{at}^2 m^*}. \tag{13}$$

In order to get an order of magnitude of R_{NTs} let us consider a cylindrical surface of Au as that studied by Van Rhee *et al* [14], with $r = 15\,nm$ and $L = 80\,nm$. For Au $r_{at} = 0.142\,nm$, $a = 0.4\,nm$ and $Z = 78$, it will be considered one electron per atom in the conduction band, $\alpha = 1$, and an effective mass $m^* = 1.1$ [17]. The following relevant values are obtained $N = 9.410^4$, $n_\varphi^{\max} = 235$ and $\Delta = 0.7\,eV$. In this case, after taking into account (10), it is found $R_{NTs} = 4.310^2\,\beta = 4.3(1–1.910^2(k_BT)^2)$. At $T = 0\,K$, $R_{NTs} = 430$ whereas at room temperature β is approximately 0.9 and $R_{NTs} = 390$.

This result can be easily extrapolated to the surface of NRs. In this case, the susceptibility ratio R_{NRs} has to take into account that all the atoms inside the NRs also contribute to the diamagnetic response. After considering that the number of atoms in the volume unite cell is 4, the total number of atoms in the NR is r/a times the number of atoms at the surface. Consequently R_{NRs}, after considering the total number of atoms in the NR becomes

$$R_{NRs} = \frac{a}{r} R_{NTs} = \frac{3ra\alpha\beta}{2Zr_{at}^2 m^*} \tag{14}$$

Since the induced magnetic moments described by (11) and (12) are larger than those associated with both Landau diamagnetism and Pauli paramagnetism of all the conduction electrons different to the surface ones, we shall disregard these two last contributions in a first order of approximation.

Relation (14) leads to a diamagnetic susceptibility of the surface electrons given by

$$\chi_d = 11.5\frac{\beta\alpha}{m^*}\chi_{at} \tag{15}$$

The experimental susceptibility measured and reported by Van Rhee *et al* [14] for his sample with the same dimensions (labeled H in [14]) is $\chi_{exp} = (14 \pm 4)\chi_{at}$. This experimental value and that derived from (15) would be in good agreement if $\frac{\beta\alpha}{m^*}$ were of the order of unity. Therefore, with the calculated β value, that varies between 1 and 0.9 as T ranges from 0 to $293\,K$, and the considered values for the effective mass $m^* = 1.1$ and of $\alpha = 1$, the calculated susceptibility accounts with surprisingly good quantitative agreement for the experimental one. The m^* value for Au surface electrons, given by $m^* = \hbar^2/2a^2b$, as derived from the experimental hopping amplitude, $b = 0.25\,eV$, measured by LaShell et *al* [18], becomes $m^* = 0.78$. Therefore, if instead of the bulk effective mass $m^* = 1.1$ one uses the experimental surface electron effective mass, the coefficient $\frac{\beta\alpha}{m^*}$ changes from 0.91 to 1.25 at $0\,K$ and from 0.82 to 1.12 at room temperature. For both cases the coefficient lies close to the unity.

It has been only considered the diamagnetic susceptibility. According to the high value of $n_\varphi^{\max}$ the paramagnetic contribution coming from unfilled Fermi level might be larger than the diamagnetic one depicted by (11). If the number of electrons at the Fermi level, N_F, is lower than the maximum allowed one, $N_F^{\max} = 2(2n_\varphi^{\max} + 2)$, the NRs will exhibit an orbital magnetic moment whose maximum possible value would depend on the coupling between electrons that should be governed by the relative strength of the exchange and spin–orbit interactions, as well as on its relative population. For non interacting electrons the maximum possible orbital

moment would be reached for half population. For this case two electrons with opposite spins could fill a half band of only positive n_φ ranging between 0 and $n_\varphi^{\max}$. For a half filled band with $n_\varphi^{\max} = 235$ the total orbital moment at room temperature could reach a value 0.1 Bohr magneton per surface atom, approximately. This effect of giant paramagnetism has been observed in thiol capped Au NPs. In this case the diamagnetism is masked by the paramagnetic component. However, if there is only one hole at the Fermi level the maximum achievable orbital moment of the surface band should be 235 Bohr magnetons that would correspond to 210^{-3} Bohr magnetons per surface atom, value that yields weak paramagnetic component. In this report we have calculated only the diamagnetic component that should correspond to the experimental susceptibility only for those samples with vanishingly small paramagnetic component. But is relevant to observe how the existence of steady currents can drive the magnetic response from paramagnetic to diamagnetic depending on the occupation of the degenerated surface Fermi level. The experimentally observed effect of capping is presumably related to the influence of binding on the occupancy of the surface Fermi level.

In conclusion, it has been calculated the diamagnetic susceptibility originated by steady currents induced by the applied magnetic field for quasi-free electrons confined in a cylindrical surface. The fraction of surface electrons, β, available to create steady currents has been estimated, as a function of the geometry of the NRs and the temperature, after analyzing the relevant features of the energy spectrum. According to (10), as the size of the sample increases β decreases but also the percentage of surface atoms decreases, consequently the magnetism of the surface approaches to that of the bulk and, moreover, its relative weight in the overall magnetic behavior becomes less relevant. The experimental results found by van Rhee et *al* [14] can be, qualitatively and quantitatively, well explained on the basis of the arguments here developed. Thus, speculative arguments based on mesoscopic fluctuations of the orbital magnetic susceptibility, never experimentally detected, should not be necessarily invoked. Finally we must add that the anomalous magnetism observed in Au NRs and NPs should be deeply associated with the electron orbital moments that are good quantum numbers for cylindrical and spherical surfaces; in contrast with the electrons confined in plane surfaces.

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